

Picloram and Aminopyralid Sorption to Soil and Clay Minerals

Brandon J. Fast, Jason A. Ferrell, Gregory E. MacDonald, L. Jason Krutz, and William N. Kline*

Research was conducted to determine picloram and aminopyralid sorption in five soils and three clay minerals and to determine if the potential for off-target movement of aminopyralid in soil is less than that of picloram. Nearly all sorption of picloram and aminopyralid occurred between 0 and 8 h, and the maximum theoretical sorption of picloram and aminopyralid were 10.3 and 15.2%, respectively. Freundlich distribution coefficients (K_f) for picloram ranged from 0.12 in a Cecil sandy loam to 0.81 in an Arredondo fine sand, while K_f values for aminopyralid ranged from 0.35 in a Cecil sandy loam to 0.96 in an Arredondo fine sand. Furthermore, K_f values of aminopyralid were higher than those of picloram in all soils tested. K_f values of picloram in clay minerals were 0.25 (kaolinite), 1.17 (bentonite), and 1,016.4 (montmorillonite), and those of aminopyralid were 5.63 (kaolinite), 2.29 (bentonite), and 608.90 (montmorillonite). It was concluded that soil sorption of aminopyralid was greater than that of picloram and that the potential for off-target movement of aminopyralid is less than that of picloram.

Nomenclature: Aminopyralid; picloram.

Key words: Freundlich distribution coefficient, herbicide adsorption, herbicide leaching, herbicide sorption kinetics.

Picloram and aminopyralid are auxin-type herbicides of the pyridinecarboxylic acid family. Picloram (Figure 1) was introduced in 1963 for the control of broadleaf weeds, including several deep-rooted perennial herbaceous species and woody brush species (Gantz and Laning 1963; Hamaker et al. 1963) and is currently labeled for use in pasture and rangeland, wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.), barley (*Hordeum vulgare* L.), and noncrop areas at application rates of 0.07 to 1.12 kg ae ha⁻¹ (Anonymous 2009). Picloram is a moderately sorbed ($K_d = 0.5$) weak acid herbicide ($pK_a = 2.3$) with a water solubility of 452 mg L⁻¹ at pH 2.68 (Osteryoung and Whittaker 1980; Senseman 2007a). Aminopyralid (Figure 1), which is structurally similar to picloram, was first registered in 2005 (USOPPEPTS 2005) and is labeled for use in range and pastureland and noncrop areas at application rates of 0.05 to 0.12 kg ae ha⁻¹ for the control of several annual and perennial herbaceous broadleaf weed species (Anonymous 2008). Aminopyralid is a weak acid herbicide ($pK_a = 2.56$) that has a water solubility of 2,480 mg L⁻¹ and is moderately sorbed ($K_d = 0.72$) (Senseman 2007b).

Picloram is relatively mobile in soil, and picloram sorption to soil and clay minerals has been the focus of numerous experiments over the past 40 yr. Light-textured soils with low organic matter (OM) content and high application rates cause picloram soil mobility to increase (Baur et al. 1972; Herr et al. 1966; Scifres et al. 1969), and the potassium salt formulation of picloram is more mobile than the triisopropanolamine salt formulation (Hunter and Stobbe 1972). In addition to the experiments that have been conducted on picloram soil mobility, numerous experiments have been conducted where picloram sorption was measured and reported in the form of the soil sorption constant (K_d) or the Freundlich distribution coefficient (K_f) (Arnold and Farmer 1979; Biggar and Cheung 1973; Farmer and Aochi 1974; Grover 1971). Among those experiments, the lowest reported K_f of picloram was 0.07 on an Ephrata sandy loam (60% sand, 32% silt, 8% clay, 0.94% OM, pH = 7.14) (Farmer and Aochi 1974), and the highest

reported K_f was 1.74 on a Palouse silt (12% sand, 61% silt, 27% clay, 3% OM, pH = 5.9) (Biggar and Cheung 1973). Additionally, picloram sorption is positively correlated to OM content (Farmer and Aochi 1974; Grover 1971; Hamaker et al. 1966) and negatively correlated to soil pH (Arnold and Farmer 1979; Biggar and Cheung 1973). Picloram's weak soil sorption, correlation between sorption and soil pH, and the resulting high degree of soil mobility can be attributed to its weak acid nature. More than half of the molecules of a weak acid compound are in the undissociated-nonionic form at pH values that are below the pK_a of the compound, and the number of molecules in the dissociated-anionic form increases as pH increases (Wauchope et al. 2002; Nicholls and Evans 1991). Because the pH of field soils is typically far above the pK_a of picloram (2.30) and aminopyralid (2.56) (Senseman 2007a, 2007b), most of those molecules are in the dissociated-anionic form when present in field soil. The dissociation of weak acid herbicide molecules in soil affects sorption because dissociated-anionic molecules are repelled by the net negative charge of soil surfaces (Green and Karickhoff 1990). Weak acid herbicides are often strongly sorbed to clay minerals because the pH at the surface of many clay minerals can be 3 to 4 pH units lower than that of the soil solution (Bailey et al. 1968; Noyan et al. 2006); therefore, molecules at clay surfaces can convert to the undissociated-nonionic form and be adsorbed to the clay surfaces via coulombic interactions.

Due to its weak soil sorption and the resulting high degree of mobility in the soil, picloram can potentially move off-target to ground and surface water in and adjacent to treated areas (Lym and Messersmith 1988; Smith et al. 1988; Wood and Anthony 1997). Despite the environmental concerns caused by off-target movement to water, picloram continues to be heavily used because of the high degree of efficacy and residual control that it provides on numerous broadleaf weed species. Aminopyralid, like picloram, is also highly efficacious on broadleaf weeds and provides residual weed control; however, aminopyralid has much lower use rates and a shorter half-life than picloram (Senseman 2007a, 2007b), which suggests that the potential for negative environmental impacts is much lower with aminopyralid than with picloram. In addition to its lower use rates and shorter soil half-life, the K_d of aminopyralid (0.72) is greater than that of picloram (0.50) (Senseman 2007a, 2007b), which suggests that aminopyralid soil sorption is greater than that of picloram. No K_f values or

DOI: 10.1614/WS-D-10-00001.1

* First, second, and third authors: Agronomy Department, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, FL 32611; fourth author, USDA-ARS Southern Weed Science Research Unit, Stoneville, MS 38776; fifth author, Dow AgroSciences, Duluth, GA 30096. Corresponding author's E-mail: bfast_an@yahoo.com

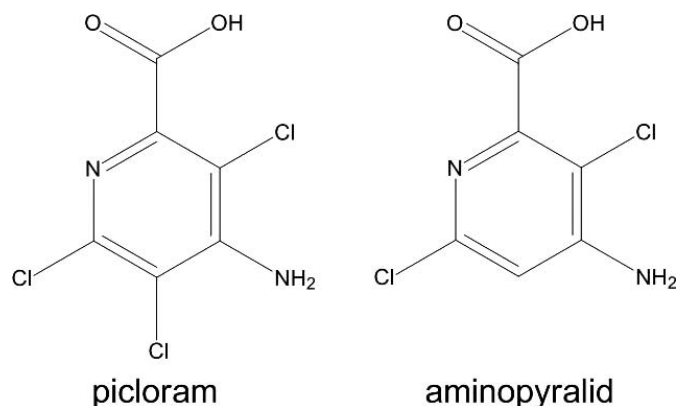


Figure 1. Chemical structures of picloram and aminopyralid.

additional published data on aminopyralid sorption relative to soil texture and OM content were found in the literature. The objective of this research was to characterize picloram and aminopyralid sorption to five soils and three clay minerals and use that information to determine if the potential for off-target movement of aminopyralid in the soil is less than that of picloram.

Materials and Methods

Sorption Kinetics. Sorption kinetics of the potassium salt formulation of picloram and aminopyralid were determined on an Arredondo fine sand (see Table 1 for soil characteristics) using the batch equilibrium method (Weber 1986). Soil was placed in 50-ml plastic centrifuge tubes (2 g tube⁻¹) and 10 ml of 0.01 M calcium chloride solution that contained either picloram or aminopyralid at concentrations of 0.1 and 1.0 g ae L⁻¹ were added to each tube. Herbicide solutions contained mixtures of either picloram plus ¹⁴C-picloram or aminopyralid plus ¹⁴C-aminopyralid.¹ The specific activity and radiochemical purity of picloram were 9.10 × 10⁸ kBq mol⁻¹ and > 99%, respectively, and the specific activity and radiochemical purity of aminopyralid were 1.01 × 10⁹ kBq mol⁻¹ and 98%, respectively. Centrifuge tubes were placed on a wrist action shaker, removed after 1, 6, 12, 24, or 48 h, and centrifuged at 3,600 × *g* for 4 min. A 2-ml aliquot of the supernatant from each centrifuge tube was added to 15 ml of liquid scintillation cocktail, and the amount of radioactivity was quantified via liquid scintillation spectrometry. Herbicide not in solution was considered sorbed; hence, the amount of herbicide sorbed was calculated by subtracting the supernatant concentration from the concentration of herbicide initially added. Test concentrations did not exceed herbicide solubility, and a preliminary quality

assurance experiment revealed that herbicide sorption to centrifuge tubes was negligible. Based on the relatively long half-lives of these compounds (Senseman 2007a, 2007b) and the report of Biggar et al. (1978) that no degradation of picloram occurred during a sorption experiment, we assumed that picloram and aminopyralid degradation would not occur in our experiments.

Sorption to Soil and Clay Minerals. Sorption of aminopyralid and picloram to five soils and three clay minerals was conducted in the same manner as the sorption kinetics experiments (see Table 1 for soil characteristics). Centrifuge tubes contained 2 g of soil or 0.15 g of clay, and herbicide concentrations added to the tubes were 0.01, 0.05, 0.1, and 1.0 g ae L⁻¹. Tubes were placed on a wrist action shaker for 24 h, and all other procedures were identical to those used in the sorption kinetics experiment.

Distribution of herbicide between the sorbed and solution phases was calculated using the Freundlich equation (Equation 1):

$$x/m = K_f C^{1/n} \quad [1]$$

Where x/m is the amount of herbicide adsorbed per weight of dry soil (mg kg⁻¹), C is the concentration of the herbicide in soil solution at equilibrium (mg L⁻¹), and K_f and n are empirical constants.

Molecular Modeling. Molecular modeling software (Argus-Lab 2004) was used to generate electrostatic potential-mapped electron density surface models of undissociated-nonionic and dissociated-anionic picloram and aminopyralid molecules. The software generated three-dimensional models of the herbicide molecules in their most logical configurations based on electron density, and a surface layer was then added to each model that displayed electronegativity colorimetrically. As others have done (Ferrell et al. 2005; Grey et al. 2000), we assumed that electronegative regions of the molecules would be repelled by negatively charged surfaces, while positively charged regions would contribute to the adsorption of the molecules to negatively charged surfaces via coulombic forces.

Statistical Analyses. Kinetics and sorption experiments were conducted twice using a completely randomized design, and each experiment contained three replications. Kinetics data were subjected to analysis of variance (SAS 2007), which revealed that the two-way interaction between experiment and herbicide concentration, the two-way interaction between experiment and time, and the three-way interaction between experiment, herbicide concentration, and time were not

Table 1. State of origin, taxonomy, and characteristics of the five soils included in this research.^a

State	Series	Taxonomy	Mineral composition					
			CEC	OM	Sand	Silt	Clay	
			pH	cmol _c kg ⁻¹	%			
Florida	Arredondo fine sand	Loamy, siliceous, semiactive, hyperthermic Grossarenic Paleudult	6.6	3.94	0.84	96.4	1.0	2.6
Georgia	Cecil sandy loam	Fine, kaolinitic, thermic Typic Kanhapludult	5.2	3.35	1.31	81.4	10.0	8.6
Kentucky	Maury silt loam	Fine, mixed, semiactive, mesic Typic Paleudalf	5.6	27.90	2.31	33.4	47.0	19.6
Mississippi	Bosket fine sandy loam	Fine-loamy, mixed, active, thermic Mollic Hapladalf	7.0	20.11	2.31	37.4	47.0	15.6
Mississippi	Sharkey clay	Very-fine, smectitic, thermic Chromic Epiaquert	6.0	11.16	1.11	24.2	23.7	52.1

^a Abbreviations: CEC, cation exchange capacity; OM, organic matter.

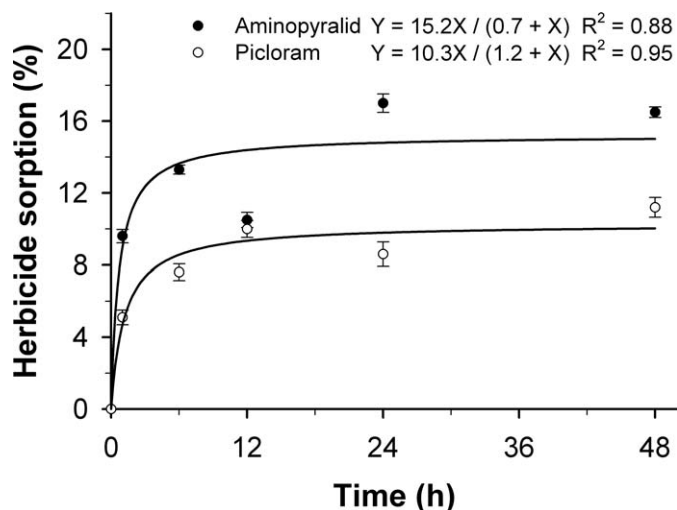


Figure 2. Picloram and aminopyralid sorption as a function of time.

significant ($P > 0.05$) for picloram and aminopyralid; therefore, sorption data were pooled across experiments and across herbicide concentrations within each herbicide. Percentage herbicide sorption was plotted against time and a hyperbolic regression model (Equation 2) was fit to the data (SigmaPlot 2006):

$$Y = aX / (b + X) \quad [2]$$

Where Y = percentage of herbicide sorbed (dependent variable), a = vertical asymptote (percentage herbicide sorption as time approaches infinity), X = time (independent variable), and b = the initial increase in Y per unit increase in X . Sorption kinetics of the two herbicides were compared using the 95% confidence intervals of the regression model parameters.

Results and Discussion

Sorption Kinetics. Picloram and aminopyralid sorption occurred in a short, initial phase of rapid sorption followed by a long phase during which sorption increased very little (Figure 2). The vertical asymptotes (maximum theoretical percentages of herbicide sorption) of picloram and aminopyralid were 10.3 and 15.2%, respectively, which indicates that aminopyralid sorption to an Arredondo fine sand is greater than that of picloram. Moreover, 46% (picloram) and 59% (aminopyralid) of the maximum theoretical sorption had occurred within 1 h, and more than 80% of the maximum theoretical sorption had occurred for both herbicides within 6 h. These results are consistent with the report of Hamaker et al. (1966) that picloram equilibrates rapidly in low OM soils.

Sorption to Soil and Clay Minerals. When herbicide sorption is described using the Freundlich equation, the empirical constant n is an indicator of the linearity of the sorption isotherm; moreover, herbicide sorption is linearly proportional to the equilibrium solution concentration when $n = 1$. When herbicide sorption is a linear function of the equilibrium solution concentration, it is appropriate to use the soil sorption constant (K_d) to describe herbicide sorption and make comparisons between treatments; however, it is more appropriate to use K_f when herbicide sorption is nonlinear

(Seybold and Mersie 1996). Because our values of n ranged from 0.62 to 1.24, we used K_f to describe picloram and aminopyralid sorption in the soils and clay minerals included in this research.

The K_f values of picloram and aminopyralid were less than 1 in all five soils included in this research (Table 2). The lowest K_f values for picloram (0.12) and aminopyralid (0.35) were observed in the Cecil sandy loam, and the highest K_f values for picloram (0.81) and aminopyralid (0.96) were observed in the Arredondo fine sand. The low K_f values (< 1) that we obtained for picloram are similar to those reported by others in several soils (Arnold and Farmer 1979; Biggar and Cheung 1973; Farmer and Aochi 1974). K_f values of aminopyralid were greater than those of picloram within each soil, which suggests that soil sorption of aminopyralid is greater than that of picloram.

Herbicide sorption varied significantly among the three clay minerals included in this research (Table 2). K_f values for picloram were 0.25 (kaolinite), 1.17 (bentonite), and 1,016.40 (montmorillonite), and K_f values for aminopyralid were 5.63 (kaolinite), 2.29 (bentonite), and 608.90 (montmorillonite). Kaolinite is a nonexpanding 1 : 1 clay (surface area = $29 \text{ m}^2 \text{ g}^{-1}$), bentonite is a 2 : 1 expanding clay (surface area = $171 \text{ m}^2 \text{ g}^{-1}$), and montmorillonite is a 2 : 1 expanding clay (surface area = $323 \text{ m}^2 \text{ g}^{-1}$) (Fushiwaki and Urano 2001). Differences in surface area and expansion between kaolinite and montmorillonite explain why sorption was several times greater in montmorillonite than kaolinite. The differences in herbicide sorption among the three clay minerals included in this research suggest that clay minerals can significantly influence the amount of herbicide sorption that occurs in soil; moreover, the importance of clay surfaces to picloram soil sorption has been previously reported (Biggar and Cheung 1973).

A correlation analysis of our data revealed that sorption was not significantly correlated to soil texture, OM content, pH, or cation exchange capacity (CEC) (Table 3), which conflicts with previous reports that picloram sorption was positively correlated to OM content (Biggar and Cheung 1973; Farmer and Aochi 1974; Grover 1971) and negatively correlated to pH (Arnold and Farmer 1979; Biggar and Cheung 1973). In addition to the correlation analysis between sorption and OM, K_{OM} values were also calculated for picloram and aminopyralid in the five soils by dividing K_f by percentage OM and multiplying by 100. If the contribution of OM to herbicide sorption was similar in the five soils, K_{OM} should not vary substantially among soils. However, K_{OM} values of the five soils included in this research were highly variable (data not shown), indicating that the contribution of OM to herbicide sorption differs among soils. The lack of correlation between herbicide sorption and soil texture, OM content, pH, and CEC indicates that additional factors or an interaction between factors influenced picloram and aminopyralid sorption. OM is not the only sorbent of herbicides in soil (Wauchope et al. 2002), and sorbents such as hydrated metal oxides and the mineral fraction of soil can contribute to picloram sorption (Hamaker et al. 1966; Cox et al. 1998). Clay minerals provide a suitable surface for weak acid herbicide sorption because their surface pH is often lower than that of the soil solution. The lower pH on the clay surface allows dissociated-anionic picloram molecules to enter the undissociated-nonionic form, which can be adsorbed to

Table 2. Freundlich equation parameters (K_f and n) for picloram and aminopyralid in the five soils and three clay minerals included in this research. All R^2 values are 0.99, and numbers in parentheses are 95% confidence intervals.

Soil/clay	Pyridinecarboxylic acid herbicide			
	Picloram		Aminopyralid	
	K_f	n	K_f	n
Arredondo fine sand	0.81 (0.78–0.84)	0.88 (0.77–0.99)	0.96 (0.94–0.98)	0.99 (0.92–1.06)
Cecil sandy loam	0.12 (0.11–0.13)	0.97 (0.88–1.06)	0.35 (0.32–0.38)	0.91 (0.58–1.24)
Maury silt loam	0.36 (0.35–0.37)	1.21 (1.10–1.32)	0.95 (0.93–0.97)	1.00 (0.95–1.05)
Bosket fine sandy loam	0.40 (0.39–0.41)	1.02 (0.92–1.12)	0.68 (0.66–0.70)	1.11 (1.01–1.21)
Sharkey clay	0.52 (0.50–0.54)	1.24 (1.09–1.39)	0.79 (0.77–0.81)	1.04 (0.97–1.11)
Bentonite	1.17 (1.05–1.28)	1.08 (0.74–1.42)	2.29 (2.17–2.41)	0.99 (0.80–1.18)
Kaolinite	0.25 (0.23–0.27)	0.62 (0.08–1.16)	5.63 (5.30–5.96)	1.05 (0.85–1.25)
Montmorillonite	1,016.40 (979.70–1,053.10)	1.12 (1.10–1.14)	608.90 (564.30–653.60)	1.03 (1.00–1.06)

the clay surfaces by coulombic forces (Biggar and Cheung 1973; Bailey et al. 1968; Noyan et al. 2006).

It has been reported that picloram sorption was positively correlated to OM content, that picloram sorption was negatively correlated to pH, and that picloram movement was greater in light-textured soils with low OM content compared to heavier soils with more OM (Arnold and Farmer 1979; Baur et al. 1972; Biggar and Cheung 1973; Farmer and Aochi 1974; Hamaker et al. 1966; Herr et al. 1966; Scifres et al. 1969). The Cecil sandy loam soil had 15% less sand, 0.47% more OM, and a pH that was 1.4 units below that of the Arredondo fine sand, which would lead one to predict that less picloram and aminopyralid sorption would occur in the Arredondo fine sand than in the Cecil sandy loam. However, K_f values of picloram and aminopyralid were higher in the Arredondo fine sand than in the Cecil sandy loam. The fact that the Cecil sandy loam is a kaolinitic soil could provide an explanation for this phenomenon. Sorption of picloram and aminopyralid to kaolinite was the lowest of the three clay minerals included in this research. Even though the Cecil sandy loam contained a greater percentage of clay, picloram and aminopyralid sorption may have been greater on the clay minerals that were present in the Arredondo fine sand. Given the differences we observed in sorption to the different clay minerals, the effect of differing clay minerals in different soils could outweigh the effect of soil texture, OM content, and pH. Results similar to ours have been reported with other weak acid herbicides; moreover, sorption of imazapyr, imazethapyr, and sulfometuron was lowest in the soils with the highest clay content (Gan et al. 1994; Wehtje et al. 1987). It should also be noted that OM can obstruct clay mineral surfaces and thus make them less available for herbicide sorption (Cox et al. 1998; Hance 1969). Another possible explanation for our results is that additional factors such as herbicide sorption to hydrated metal oxides may have contributed to picloram and aminopyralid sorption.

Table 3. Pearson correlation coefficients between picloram and aminopyralid sorption (K_f) and sand, silt, clay, pH, OM, and CEC of the five soils included in this research.

Soil property ^a	Picloram K_f	Aminopyralid K_f
Sand	0.21 ($P = 0.73$)	−0.19 ($P = 0.76$)
Silt	−0.32 ($P = 0.59$)	0.18 ($P = 0.77$)
Clay	−0.001 ($P = 0.99$)	0.13 ($P = 0.84$)
OM	−0.45 ($P = 0.45$)	0.04 ($P = 0.95$)
pH	0.64 ($P = 0.25$)	0.41 ($P = 0.50$)
CEC	−0.18 ($P = 0.78$)	0.41 ($P = 0.49$)

^a Abbreviations: CEC, cation exchange capacity; OM, organic matter.

Molecular Modeling. Herbicide molecules that contain highly electronegative regions are repelled by the net negative charge of soil surfaces. In the undissociated-nonionic form, most regions of picloram and aminopyralid molecules are positively charged; however, small regions of high electronegativity exist on the nitrogen atom of the pyridine ring and on the oxygen atoms of the carboxyl group (Figure 3). All regions of picloram and aminopyralid molecules are highly electronegative when present in the dissociated-anionic form, except for the hydrogen atoms on the amino group. Because the pH of typical field soils is greater than the pK_a values of those herbicides, the majority of picloram and aminopyralid molecules in soil solution are in the dissociated-anionic form; this helps explain why these herbicides are weakly sorbed to soil. Decreasing pH can cause picloram and aminopyralid molecules to change from the dissociated-anionic to undissociated-nonionic form, which explains why the low surface pH of clay minerals can increase the soil sorption of these herbicides.

Picloram and aminopyralid are weakly sorbed to soils as a result of their weak acid nature, and the potential for these herbicides to move off-target is greater than that of many other herbicides. K_f values of aminopyralid and picloram were less than 1.00 in this research, and reported K_f values of atrazine and sulfentrazone were 11.08 and 3.35, respectively (DeSutter et al. 2003; Reddy and Locke 1998). Although there is potential for both picloram and aminopyralid to move off-target in the soil, K_f values of aminopyralid were significantly greater than those of picloram for the five soils included in this research. This indicates that there is less potential for off-target movement of aminopyralid in the soil compared to that of picloram. Sorption to clay minerals varied by an order of magnitude among the three clay minerals included in this research, which suggests that the type of clay mineral present in soils can affect picloram and aminopyralid sorption. Picloram and aminopyralid sorption to the five soils included in this research was not significantly correlated to soil texture, OM content, pH, or CEC; therefore, it was concluded that additional factors such as the type of clay minerals present in the soil or herbicide sorption to hydrated metal oxides have a significant influence on picloram and aminopyralid sorption to soil. Models of picloram and aminopyralid molecules with a colorimetric display of electronegativity indicate that herbicide molecules in the dissociated-anionic form are unlikely to be adsorbed because they would be repelled by the net negative charge of soil surfaces; moreover, most molecules are in the dissociated-anionic form at the pH values of typical field soils. The maximum labeled application rate of aminopyralid is less

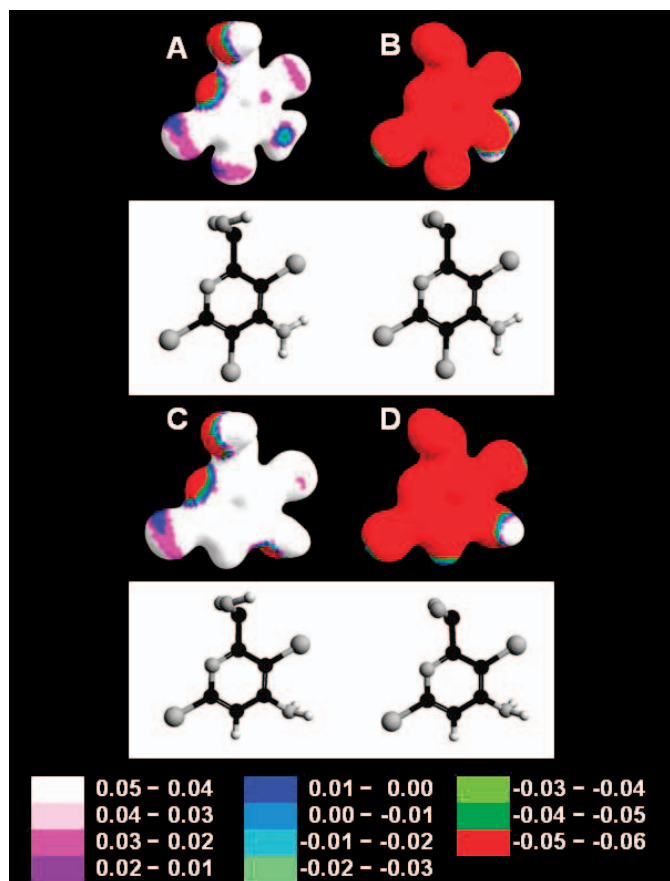


Figure 3. Molecular models of picloram in the undissociated-nonionic (A) and dissociated-anionic (B) forms and aminopyralid in the undissociated-nonionic (C) and dissociated-anionic (D) forms. Ball-and-stick models directly below the surface-mapped molecules indicate the configuration of the atoms within the surface-mapped models.

than that of picloram (Anonymous 2008; Anonymous 2009a), the average half-life of aminopyralid (34.5 d) is less than that of picloram (90 d) (Senseman 2007a, 2007b), and aminopyralid soil sorption was greater than that of picloram. The low K_f values of picloram and aminopyralid indicate that there is potential for off-target movement of these compounds in the soil. Additionally, the higher K_f values of aminopyralid compared to those of picloram indicate that the potential for aminopyralid to move off-target is slightly less than that of picloram.

Sources of Materials

¹ Picloram plus ¹⁴C-picloram and aminopyralid plus ¹⁴C-aminopyralid, Dow AgroSciences, Indianapolis, IN.

Literature Cited

- Anonymous. 2008. Milestone® herbicide product label. Dow AgroSciences Publication No. D02-879-002. Indianapolis, IN: Dow AgroSciences. 9 p.
- Anonymous. 2009. Tordon® 22K herbicide product label. Dow AgroSciences Publication No. D02-111-013. Indianapolis, IN: Dow AgroSciences. 14 p.
- ArgusLab. 2004. ArgusLab Version 4.0.1. Seattle, WA: Planaria Software LLC.
- Arnold, J. S. and W. J. Farmer. 1979. Exchangeable cations and picloram sorption by soil and model adsorbents. *Weed Sci.* 27:257–262.
- Bailey, G. W., J. L. White, and I. Rothberg. 1968. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.* 32:222–234.
- Baur, J. R., R. D. Baker, R. W. Bovey, and J. D. Smith. 1972. Concentration of picloram in the soil profile. *Weed Sci.* 20:305–309.
- Biggar, J. W. and M. W. Cheung. 1973. Adsorption of picloram (4-amino-3,5,6-trichloropicolinic acid) on Panoche, Ephrata, and Palouse soils: a thermodynamic approach to the adsorption mechanism. *Soil Sci. Soc. Am. Proc.* 37:863–868.
- Biggar, J. W., U. Mingelgrin, and M. W. Cheung. 1978. Equilibrium and kinetics of adsorption of picloram and parathion with soils. *J. Agric. Food Chem.* 26:1306–1312.
- Cox, L., W. C. Koskinen, R. Celis, P. Y. Yen, M. C. Hermosin, and J. Cornejo. 1998. Sorption of imidacloprid on soil clay mineral and organic components. *Soil Sci. Am. J.* 62:911–915.
- DeSutter, T. M., S. A. Clay, and D. E. Clay. 2003. Atrazine sorption and desorption as affected by aggregate size, particle size, and soil type. *Weed Sci.* 51:456–462.
- Farmer, W. J. and Y. Aochi. 1974. Picloram sorption by soils. *Soil Sci. Soc. Am. Proc.* 38:418–422.
- Ferrell, J. A., W. K. Vencill, K. Xia, and T. L. Grey. 2005. Sorption and desorption of flumioxazin to soil, clay minerals, and ion-exchange resin. *Pest Manag. Sci.* 61:4046.
- Fushiwaki, Y. and K. Urano. 2001. Adsorption of pesticides and their biodegraded products on clay minerals and soils. *J. Health Sci.* 47:429–432.
- Gan, J., M. R. Weimer, W. C. Koskinen, D. D. Buhler, D. L. Wyse, and R. L. Becker. 1994. Sorption and desorption of imazethapyr and 5-hydroxyimazethapyr in Minnesota soils. *Weed Sci.* 42:92–97.
- Gantz, R. L. and E. R. Laning. 1963. Tordon for the control of woody rangeland species in the western United States. *Down to Earth* 19(3):10–13.
- Green, R. E. and S. W. Karickhoff. 1990. Sorption estimates for modeling. Pages 79–102 in H. H. Cheng, ed. *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*. Madison, WI: Soil Science Society of America.
- Grey, T. L., R. H. Walker, G. R. Wehtje, J. Adams, Jr., F. E. Dayan, J. D. Weete, H. G. Hancock, and O. Kwon. 2000. Behavior of sulfentrazone in ionic exchange resins, electrophoresis gels, and cation-saturated soils. *Weed Sci.* 48:239–247.
- Grover, R. 1971. Adsorption of picloram by soil colloids and various other adsorbents. *Weed Sci.* 19:417–418.
- Hamaker, J. W., C. A. Goring, and C. R. Youngson. 1966. Sorption and leaching of 4-amino-3,5,6-trichloropicolinic acid in soils. *Adv. Chem. Ser.* 60:23–37.
- Hamaker, J. W., H. Johnston, R. T. Martin, and C. T. Redeman. 1963. A picolinic acid derivative: a plant growth regulator. *Science* 141:363.
- Hance, R. J. 1969. Influence of pH, exchangeable cation, and the presence of organic matter on the adsorption of some herbicides by montmorillonite. *Can. J. Soil Sci.* 49:357–364.
- Herr, D. E., E. W. Stroube, and Dale. A. Ray. 1966. The movement and persistence of picloram in soil. *Weeds* 14:248–250.
- Hunter, J. H. and E. H. Stobbe. 1972. Movement and persistence of picloram in soil. *Weed Sci.* 20:486–488.
- Lym, R. G. and C. G. Messersmith. 1988. Survey for picloram in North Dakota groundwater. *Weed Technol.* 2:217–222.
- Nicholls, P. H. and A. A. Evans. 1991. Sorption of ionisable organic compounds by field soils. Part 1: acids. *Pestic. Sci.* 33:319–330.
- Noyan, H., M. Önal, and Y. Sarikaya. 2006. The effect of heating on the surface area, porosity and surface acidity of a bentonite. *Clays Clay Miner.* 54:375–381.
- Osteryoung, J. and J. W. Whittaker. 1980. Picloram: solubility and acid-base equilibria determined by normal pulse polarography. *J. Agric. Food Chem.* 28:95–97.
- Reddy, K. N. and M. A. Locke. 1998. Sulfentrazone sorption, desorption, and mineralization in soils from two tillage systems. *Weed Sci.* 46:494–500.
- [SAS] Statistical Analysis Systems. 2007. Software Version 9.2. Cary, NC: Statistical Analysis Systems Institute.
- Scifres, C. J., O. C. Burnside, and M. K. McCarty. 1969. Movement and persistence of picloram in pasture soils of Nebraska. *Weed Sci.* 17:486–488.
- Senseman, S. A., ed. 2007a. *Herbicide Handbook*. 9th ed. Champaign, IL: Weed Science Society of America. Pp. 353–356.
- Senseman, S. A., ed. 2007b. *Herbicide Handbook*. 9th ed. Champaign, IL: Weed Science Society of America. Pp. 331–332.
- Seybold, C. A. and W. Mersie. 1996. Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine, hydroxyatrazine, and metolachlor in two soils from Virginia. *J. Environ. Qual.* 25:1179–1185.
- SigmaPlot. 2006. Software Version 10.0. Chicago, IL: Systat Software, Inc.
- Smith, A. E., D. Waite, R. Grover, L. A. Kerr, L. J. Milward, and H. Sommerstad. 1988. Persistence and movement of picloram in a northern Saskatchewan watershed. *J. Environ. Qual.* 17:262–268.
- [USOPPEPTS] United States Office of Prevention, Pesticides, Environmental Protection, and Toxic Substances. 2005. Aminopyralid Pesticide Fact Sheet.

- <http://www.epa.gov/opprd001/factsheets/aminopyralid.pdf>. Accessed: May 8, 2009.
- Wauchope, R. D., S. Yeh, J. B. Linders, R. Kloskowski, K. Tanaka, B. Rubin, A. Katayama, W. Kordel, Z. Gerstl, M. Lane, and J. B. Unsworth. 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations, and reliability. *Pest Manag. Sci.* 58:419–445.
- Weber, J. B. 1986. Herbicide adsorption by solids from solution. Pages 174–179 in N. D. Camper, ed. *Research Methods in Weed Science* Southern Weed Science Society: Champaign, IL.
- Wehtje, G., R. Dickens, J. W. Wilcut, and B. F. Hajek. 1987. Sorption and mobility of sulfometuron and imazapyr in five Alabama soils. *Weed Sci.* 35:858–864.
- Wood, J. A. and D.H.J. Anthony. 1997. Herbicide contamination of prairie springs at ultratrace levels of detection. *J. Environ. Qual.* 26:1308–1318.

Received January 4, 2010, and approved June 22, 2010.